SEPARATION OF POLYBASIC ACIDS FROM THE OXIDATIVE CLEAVAGE OF SYNTHETIC RUBBER

BY

JOHN CADWALLADER RICHARDS

B.A., Princeton University, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

The most commonly used chemical method for studying the structure of diene polymers and copolymers involves oxidative scission of the double bonds in the polymer and separation and identification of the resulting fragments. In most cases, the oxidizing agent will tend to carry these fragments past the aldehyde structure, so the most convenient method for obtaining a good yield of scission products is to operate under conditions such that the products will be carboxylic acids.

One of the major difficulties encountered in such structure studies is the problem of separating the acids. This is an especially difficult task in the case of acids obtained from oxidative cleavage of GR-S or similar polymers of butadiene and styrene, since many of the phenyl-containing acids and their esters are so non-volatile that separation of more than a few of the lower molecular weight acids by fractional distillation of their esters is out of the question.

It was the purpose of our present researches to devise a technique for separating these high-boiling acids in such a manner that they might be identified and quantitatively estimated. The method which was chosen was fractional extraction, a powerful tool for separating small amounts of volatile or non-volatile materials in rather simple equipment.

Discussion Of Results

Distribution coefficients of a number of mono- and polybasic acids between water and various organic solvents have been determined. It was found that the extracting solvents could be arranged in an order of increasing effectiveness and that the acids could also be arranged in a definite order of relative

affinity for the aqueous phase. The order in which the solvents may be arranged, proceeding from the weakest to the strongest, is as follows:

Skellysolve B (b.p. 60-65°)
Carbon Tetrachloride
Benzene
Chloroform
Diisopropyl Ketone
Butyl Acetate
Ethyl Ether
Methyl Isobutyl Ketone
Ethyl Acetate
Methyl Propyl Ketone = Methyl Ethyl Ketone = Cyclohexanone = *n*-Butanol

The order in which the polybasic acids fall, beginning with those which favored the water layer the most strongly, is as follows:

Oxalic Acid
Citric Acid
Malonic Acid
β-Carboxyadipic Acid
Succinic Acid
Glutaric Acid
Adipic Acid
Fumaric Acid
Pimelic Acid
Suberic Acid
β-Phenyladipic Acid
Azeleic Acid
Sebacic Acid

For the monobasic acids tested, the order runs as follows:

Formic Acid
Acetic Acid
Propionic Acid
Butyric Acid
Benzoic Acid

It has been shown by experiments with several of these acids that the distribution of a dibasic acid among the funnels of a fractional extraction is approximately that calculated from the distribution coefficient.

The feasibility of using fractional extraction to separate acids has been demonstrated in the case of a mixture of succinic, fumaric, and benzoic acids, whose esters boil so close to each other that separation by distillation would be almost impossible.

A simple, automatic, glass apparatus for carrying out the process of fractional extraction has been developed and tested.

The fractional extraction technique has been applied to acids derived by ozonolysis from a sample of 50/50 butadiene/styrene copolymer. It was possible to remove substantially all of the phenyl containing acids from the water soluble acids by fractional extraction between water and ether. On further fractionation of the ether soluble material between water and chloroform, two fractions were isolated. One consisted of β-phenyladipic acid and the other was a dark oil which had a high neutralization equivalent and showed strong ultraviolet absorption at 2400 A.

Fractional extraction of the water insoluble acids between water and chloroform resulted in removal into the aqueous layers of a fraction whose neutralization equivalent suggested the presence of β-phenyladipic acid. Fractionation of the water insoluble acids between carbon tetrachloride and 75 per cent aqueous methanol resulted in migration of most of the acidic material into the aqueous fractions. The neutralization equivalent of the acids in the first aqueous fraction suggested the presence of considerable diphenylsuberic acid. The portion which remained in the first carbon tetrachloride fraction was almost neutral.

VITA

The author was born in Yonkers, New York, on September 10, 1920. He attended the public schools of that city and graduated from the Roosevelt High School in June of 1938. In September of that year he entered Princeton University, from which he received the degree of Bachelor of Arts in Chemistry in June of 1942. From that date until August of 1946 he was employed as a chemist and then as a research chemist by the Pioneering Research Section, Technical Division, Rayon Department of E. I. duPont de Nemours and Company at Buffalo, New York. In September, 1946, he entered the graduate school of the University of Illinois. Since that date, he has been employed as a Special Research Assistant on the Rubber Research Program at the University.

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